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Kinetics and Prediction of Hydrogen Outgassing From Lithium Hydride

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THE MOISTURE OUTGASSING PROCESS IN A VACUUM/DRY ENVIRONMENT

In most industrial or device applications, LiH is placed in either an initially dry or a vacuum environment with other materials that may release moisture slowly over many months, years, or even decades. In such instances, the rate of hydrogen outgassing from the reaction of LiH with H_2O can be reasonably approximated by the rate at which H_2O is released from the moisture containing materials.

In a vacuum or dry environment, LiOH decomposes slowly with time into Li_2O even at room temperature [1-3] according to:

$$2LiOH(s) \rightarrow Li_2O(s) + H_2O(g) \quad (1)$$

The kinetics of the decomposition of LiOH depends on the dryness/vacuum level and temperature. It was discovered by different workers that vacuum thermal decomposition of bulk LiOH powder (grain sizes on the order of tens to hundreds of micrometers) into Li_2O follows a reaction front moving from the surface inward [2,3].

Due to stress at the LiOH/vacuum interface and defective and missing crystalline bonding at surface sites, lattice vibrations at the surfaces/interfaces of most materials are at frequencies different than those in the bulk [4], a phenomenon observed in most solids. The chemical reactivity and electronic properties at surfaces and interfaces of materials are also different than those in the bulk [4]. It is, therefore, expected that the amount of energy required to break bonds at the LiOH/vacuum interface is not as large as in the bulk. In addition, in an environment where there is a moisture sink or in the case of a continuously pumped vacuum chamber, H_2O vapor is continuously removed and LiOH decomposes into Li_2O from the LiOH/vacuum interface (where it is thermally less stable) inward according to reaction (1) in an effort to maintain the equilibrium H_2O vapor pressure at the sample/vacuum interface.

In a closed system containing both LiH and LiOH, the H_2O released from the decomposition of LiOH reacts with LiH to form hydrogen gas according to the following reaction:

$$2LiH(s) + H_2O(g) \rightarrow Li_2O(s) + 2H_2(g) + heat \quad (2)$$

Such is the case of vacuum thermal decomposition of a corrosion layer previously grown on top of a LiH substrate. Here, the huge H_2O concentration gradient across the Li_2O buffer layer in between the hydrophilic LiH substrate and LiOH, coupled with the defective nature of LiOH at surfaces/interfaces as discussed above, effectively lowers the energy barrier for LiOH decomposition here in comparison with bulk LiOH and turns the LiH substrate into an effective moisture pump [5-6]. As a result, in the case of vacuum thermal decomposition of LiOH on top of a LiH substrate, the LiOH decomposition front starts at the LiH/Li_2O/LiOH interface. As a function of increasing time and temperature, the Li_2O layer in between LiH and LiOH gets thicker, causing the energy barrier for the

LiOH decomposition at the LiOH/Li_2O/LiH interface to increase, and eventually LiOH at the LiOH/vacuum interface also starts to decompose into Li_2O for reasons described in the previous paragraph. Thereafter, the Li_2O fronts keep moving inward from all directions until all the LiOH is gone. This vacuum thermal decomposition process of LiOH previously grown on top of a LiH substrate is illustrated in the cartoon of fig. 1.

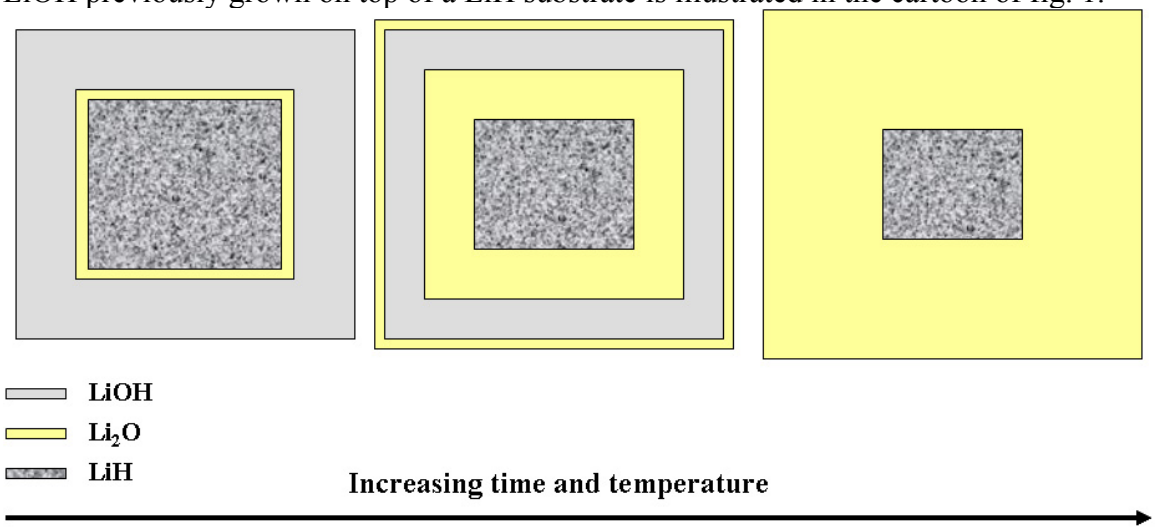

Fig. 1

OUTGASSING KINETIC MEASUREMENT AND PREDICTION

Hydrogen outgassing from the LiH/Li_2O/LiOH system was investigated mainly by the technique of temperature programmed reaction (TPR) and the details were reported elsewhere [6]. Kinetic measurements show that the activation energy for the vacuum thermal decomposition of LiOH starts out at a low value of ~ 88 kJ/mol for interfacial LiOH (LiOH within a 60 nm distance from the LiH/Li_2O interface). This activation energy barrier increases to an intermediate value of ~ 117 kJ/mol for surface LiOH (LiOH within a 34-68 nm distance from the LiOH/vacuum interface) and ultimately to a value above 134 kJ/mol for bulk LiOH. Kinetic predictions based on the measured kinetics reveal that in a dry/vacuum environment, LiOH in the corrosion layer near the LiH/Li_2O interface and near the LiOH/vacuum interface slowly decompose over many years and decades, respectively, even at room temperature into lithium oxide, releasing water vapor which then reacts with the lithium hydride substrate to form hydrogen gas. The outgassing associated with the vacuum thermal decomposition of LiOH into Li_2O is dependent on the LiOH corrosion layer thickness and baking treatments, and is directly proportional to the total LiH geometrical surface area.

A comparison between experimental isothermal hydrogen outgassing from fresh LiH, with a total geometrical surface area of 0.0190 m^2, and an outgassing prediction based on the model-independent kinetic analysis for fresh LiH, with a similar surface area, at 343 K is presented in Fig. 2(a). Figs. 2(b), (c) and (d) show comparisons between experimental isothermal hydrogen outgassing from baked LiH, with a total geometrical surface area of 0.0205 m^2, and outgassing predictions based on the model-independent kinetic analysis for baked LiH at 348.7 K, 330.1 K and 315.5 K, respectively. The heavy lines indicate experimental isothermal hydrogen outgassing data while the lighter bands

are predicted from the isoconversional kinetic analysis of TPR spectra. Despite scatter in the experimental isothermal outgassing curves, experimental and predicted curves are in good agreement.

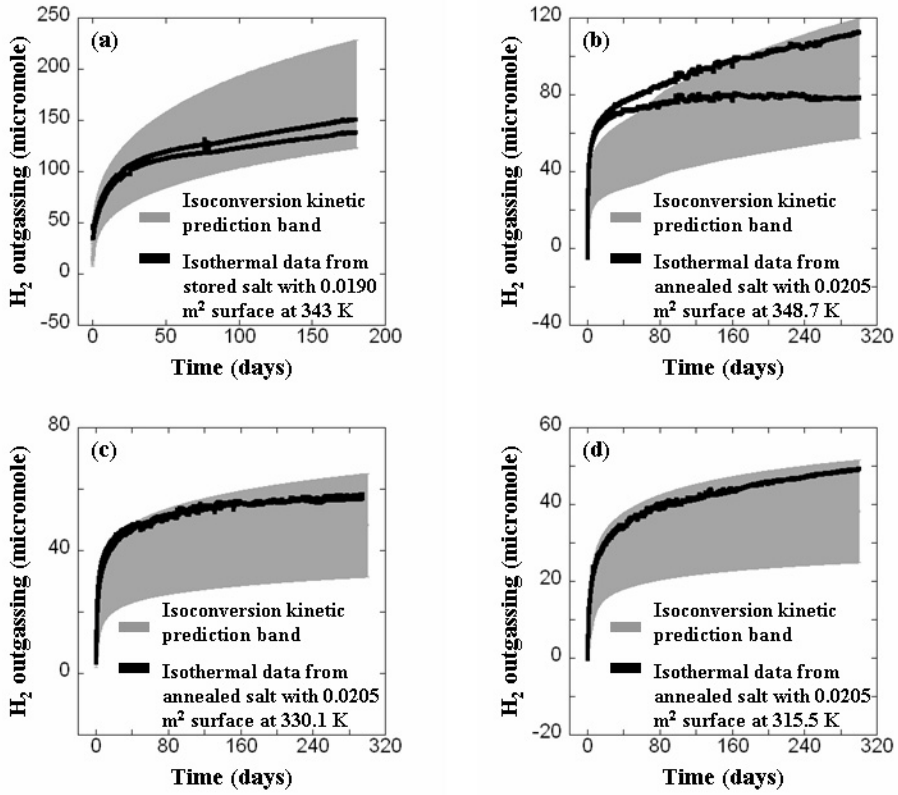

Fig. 2

Given the likely differences in preparation conditions and variations in LiH sample treatment between the TPR and isothermal experiments, it is remarkable that the isothermal data falls within the kinetic prediction bounds and, more importantly, that the curve shapes are well represented, adding credence to the kinetic prediction method presented here.

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